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Conductivity and Dynamic Mechanical Studies of PVC/PEMA Blend Polymer Electrolytes

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Keywords: polymer blends, PVC, PEMA, EIS, DMTA.

Abstract. The ionic conductivity and mechanical properties of poly (vinyl chloride) (PVC)/poly (ethyl methacrylate) (PEMA) polymer blends containing $LiN(CF_3SO_3)_2$ as doping salt has been studied using electrical impedance spectroscopy (EIS) and Dynamic Modulus Analysis (DMA) as a function of polymer blend ratios and lithium salt concentration. The film with PVC/PEMA composition of 65:35 obtained the highest conductivity with good transparency. DMA showed that both the storage modulus (E') and the glass transition temperature (T_g) of the PVC/PEMA is increased with PEMA concentration. In the case of PVC/PEMA-$LiN(CF_3SO_2)_2$ films, the conductivity was found to increase with concentration of salt added with a maximum in conductivity at 35 wt.% $LiN(CF_3SO_2)_2$. The T_g values of the doped films was found to increase with concentration of salt such that the film with the highest conductivity value has the highest T_g.

Introduction

PVC is a product based on the earth's natural resources. Nowadays, PVC is an extremely cost effective polymer in comparison to other plastics with high degree of versatility and processing possibilities [1]. Polymer blending is known to be a solution to poor mechanical strength of polymer electrolytes. Proof of this was demonstrated by a few research groups. Rhoo et.al [2] demonstrated this by blending PVC with PMMA. In their work, the mechanical strength of PVC/PMMA blend electrolytes was imparted by the PVC-rich phase. However, increasing the PVC content led to a decrease in the ionic conductivity values. The mechanical strength of PVC/PEMA blend polymer electrolytes has also been studied and was found to be higher than that of PVC/PMMA [3]. This was attributed to the elongation strength of PEMA which was higher than PMMA while its T_g was lower compared to PMMA [4, 5]. In this study physical blending between PVC/PEMA is studied. The effect of blending on the ionic conductivity is investigated and is correlated to its mechanical strength. The effect of addition of inorganic salt to the blend in terms of the parameters mentioned earlier is also studied.

Experimental

PVC with M_w=233,000 g mol^{-1}, PEMA with M_w= 515,000 g mol^{-1} and $LiN(CF_3SO_2)_2$ were all purchased from Sigma-Aldrich, USA. All polymers in various wt. % concentrations were dissolved in anhydrous tetrahydrofuran (THF) separately. They were then mixed and stirred continuously with a magnetic stirrer for several hours at room temperature to obtain a homogenous solution. The solutions were then cast into glass dishes and allowed to dry in an evacuated glove box using nitrogen gas. The films were formed after several days and kept dry in a dessicator for further characterizations. In the preparation of PVC/PEMA-$LiN(CF_3SO_2)_2$ films, the PVC/PEMA sample

with the highest conductivity value was added with different concentrations of $LiN(CF_3SO_2)_2$ as a doping salt. The above method was repeated to prepare the doped films. All samples were characterized by Electrochemical Impedance Spectroscopy (EIS) using HIOKI 3532-50 LCR Hi-Tester and Dynamic Mechanical Thermal Analysis (DMTA) by PERKIN ELMER DMA 8000.

Results and discussion

Conductivity measurement

The conductivity of PVC/PEMA blend versus concentration of PEMA at room temperature is depicted in Fig. 1. The conductivity of the blends increases with addition of PEMA up to a maximum at 35wt. % of PEMA after which the conductivity decreases with higher concentrations of PEMA. The maximum conductivity value is 4.74×10^{-10} S/cm for the composition with PVC (65wt. %): PEMA (35wt. %).

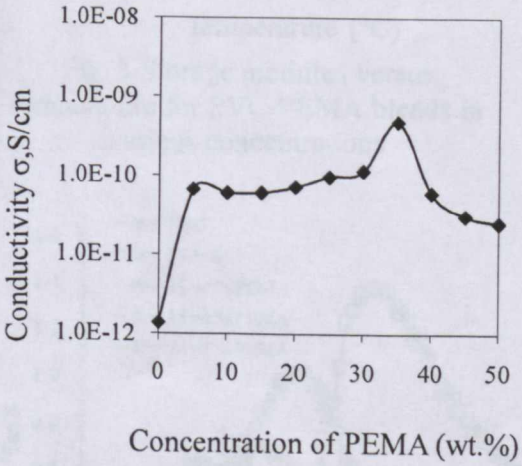

Fig. 1 Variation of conductivity with concentration of PEMA

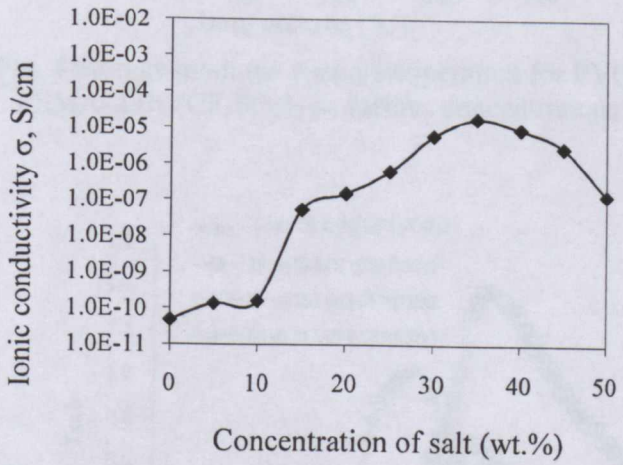

Fig. 2 Variation of conductivity with concentration of $LiN(CF_3SO_2)_2$

The effect on the conductivity upon addition of salt, $LiN(CF_3SO_2)_2$ to PVC: PEMA (65. wt%: 35. wt %) is shown in Fig. 2. The variation in conductivity with salt have the same pattern as that of Fig. 1 where the ionic conductivity increases as the salt concentration increases up to 35 wt. % of salt concentration and decreases thereafter. The maximum ionic conductivity obtained at 35 wt. % of $LiN(CF_3SO_2)_2$ is 1.75×10^{-5} S/cm. The increase in conductivity with salt concentration is attributed to the increasing number of ion dissociated from salt in the amorphous phase of PVC [7]. This is consistent with the work reported by A. M. Stephan et al. [8]. The decrease in ionic conductivity after the maximum could be attributed to the decrease in the number of ions which is caused by ion association due to the presence of a large number of ions [9].

Dynamic mechanical measurement

Dynamic storage modulus (E') of PVC/PEMA blends is shown in Fig. 3. Pure PVC and PEMA have values of E' of about 3.77×10^8 and 3.51×10^8 Pa respectively at 40°C. When PEMA is added to PVC, the E' value increases to about 1.29×10^9 Pa for PVC/PEMA concentration of 65/35 wt %. The increase in the storage modulus indicates that the two polymer phases are distributed uniformly to give synergy to the mechanical strength [10]. This shows that blending enhances the mechanical strength due to the rigidity imparted by PVC. This increase is also attributed to the increase in molecular weight when the two polymers are blended due to intermolecular interaction between the carbonyl group of PEMA and the C-Cl group of PVC [11]. As the temperature increases, the modulus value decreases in all cases and a sharp decrease is observed in the temperature range of 75°C to 95°C. Pure PEMA exhibits a decrease in storage modulus at relatively high temperature (70°C) when compared to pure PVC (60°C). Also it is obvious from the plot that PEMA exhibits

both α-relaxation corresponding to T_g and secondary relaxation of the glassy state where as the blends and pure PVC only exhibit α-transitions [12].

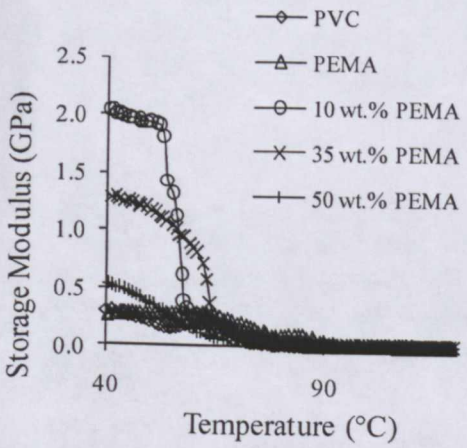

Fig. 3 Storage modulus versus temperature for PVC-PEMA blends in various concentrations

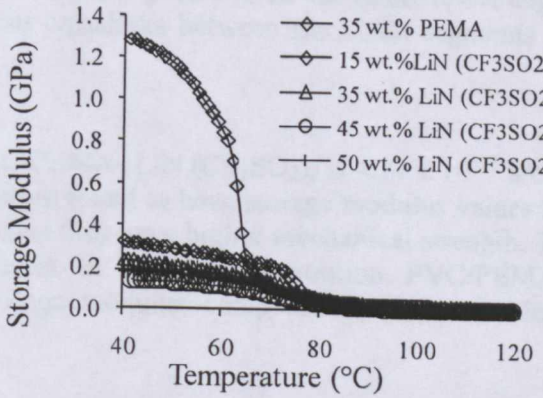

Fig. 4 Storage modulus versus temperature for PVC-PEMA- LiN $(CF_3SO_2)_2$ in various concentrations

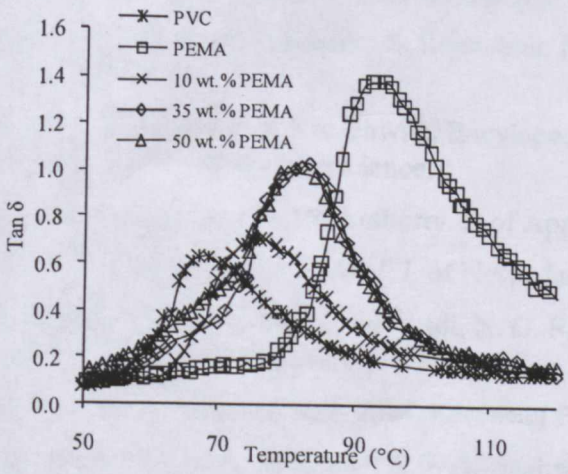

Fig 5 Tan δ versus temperature for PVC-PEMA blends at various blend ratios

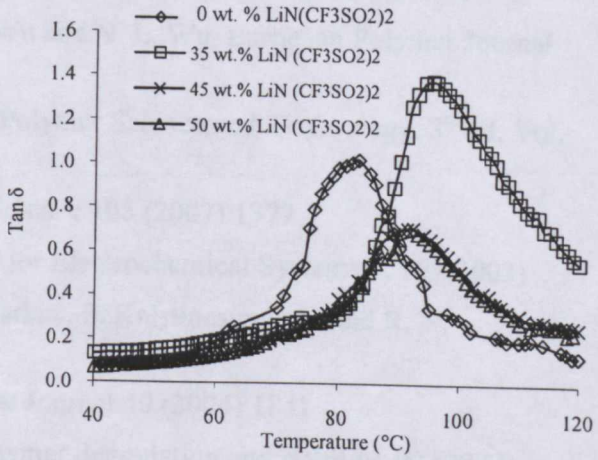

Fig 6 Tan δ versus temperature for PVC-PEMA-LiN $(CF_3SO_2)_2$ films

Fig. 4 shows the graph of storage modulus (E') for PVC/PEMA-LiN$(CF_3SO_2)_2$ films versus temperature. The addition of salt into the blend causes the storage modulus to decrease to about 1.31×10^8 Pa (for 35 wt % LiN$(CF_3SO_2)_2$) when compared to the undoped blend. The lower storage modulus for the doped system indicates that the system with lithium salt is easily deformed by an applied load compared to undoped system. This means that the stiffness of the PVC/PEMA blend have decreased when LiN$(CF_3SO_2)_2$ is added [13].

Fig. 5 and 6 depicts the variation of tan δ with temperature for PVC/PEMA blend and PVC/PEMA- LiN $(CF_3SO_2)_2$ films respectively. Tan δ of pure PEMA as seen in Fig. 5 is gradually reduced with addition of PVC and vice versa. This indicates that PEMA is transformed from viscous behavior to elastic behavior [10]. The elastic moduli values of these blends are therefore intermediate between those of neat PVC and PEMA which indicates that there are specific interactions between PVC and PEMA [13]. T_g values obtained from Fig. 5 were found to increase with higher PEMA concentration.

In the case of doped films, the values of tan δ increases when 35 wt % of salt is added and decreases thereafter indicating that the films have changed from a more viscous to a more elastic behavior. In addition, the T_g value for the film with 35 wt. % of salt is 95°C which is an increase

when compared to the T_g value of 81°C for PVC/PEMA (65. wt%/35. wt %). Since T_g is a measure of chain flexibility, this means that the highest conducting film with salt has less segmental motion and is therefore viscous. The increase in T_g with addition of salt is consistent with the works reported by several workers [14, 15]. The increase in T_g is expected to be due to the lower degree of chain movement due to the formation of transient crosslinks between the chain segments of the polymer [16, 17].

Conclusion

The highest conductivity for PVC/PEMA and PVC-PEMA- LiN $(CF_3SO_2)_2$ is 4.74 x 10^{-10} S/cm and 1.75 × 10^{-5} S/cm respectively. PVC/PEMA films were found to have storage modulus values higher than that of pure PVC and pure PEMA indicating that they have higher mechanical strength. The T_g values of the blends were also higher with increase in PEMA concentration. PVC/PEMA-LiN $(CF_3SO_2)_2$ films were found to have lower storage modulus compared to the pure blend of PVC/PEMA.

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The Investigation on Ionic Conduction of PEMA Based Solid Polymer Electrolytes

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Keywords: polymer electrolytes. conductivity, XRD, scherrer length, dielectric constant

Abstract. Solid polymer electrolytes comprising of various weight ratios of poly(ethyl methacrylate) (PEMA) and lithium perchlorate ($LiClO_4$) salt were prepared via solution casting technique using N,N-Dimethylformamide (DMF) as the solvent. The conductivity values of the electrolytes were determined utilizing Solatron 1260. The highest conductivity obtained is in the order of 10^{-6} S cm^{-1}. Structural properties of the electrolytes were investigated by X-ray diffraction and the results show that the highest conducting film is the most amorphous.

Introduction

Polymer is a material constructed of a large number of molecules that is formed from the repetition of small and simple chemical units called monomer bonded by covalent bonds. Most polymers have no ability to conduct electricity. Besides its poor electrical conductivity property, for the last five decades, ion conducting polymers has been synthesized via dissolving inorganic salt into its matrix. Polymer electrolytes possess various advantages such as solvent free condition, structurally stable, easy for any process and mobileable [1]. Various kinds of polymers have been chosen as host such as PEO [2], PPO [3], PVA [4,5], PVC [6], PVDF [7] and PMMA [8]. In this work, the potential of PEMA as a polymer host is investigated. $LiClO_4$ is added as the doping salt. PEMA was chosen as host as it exists in amorphous form [9]. By incorporating $LiClO_4$ in to PEMA, it was hoped that the media for ion mobilities will be enhanced.

Experimental

Various weight percentages, wt% of $LiClO_4$ was dissolved into commercially available PEMA (M_w = 215,000) employing DMF as solvent. The films were cast using the solution casting method. The cast films were subjected to EIS (Solatron 1260) and XRD analysis (LabX XRD 6000) for impedance and structural studies respectively.

Results and Discussion

Fig. 1 depicts the X-Ray diffractograms of PEMA-$LiClO_4$ films at various concentrations. For pure PEMA, the XRD pattern obtained in this work is similar to that obtained by Rajendran et.al [10] that is a small peak appeared at $2\theta \approx 29.5^0$. PEMA-$LiClO_4$ diffractograms show a few peaks due to the presence of $LiClO_4$ and is prominent for the film with 30 wt% $LiClO_4$. Such observation is most possibly due to the uncomplexed salt or ion aggregation of the salt. For 30 wt% $LiClO_4$ the degree of uncomplexed salt or ion aggregation is the highest.

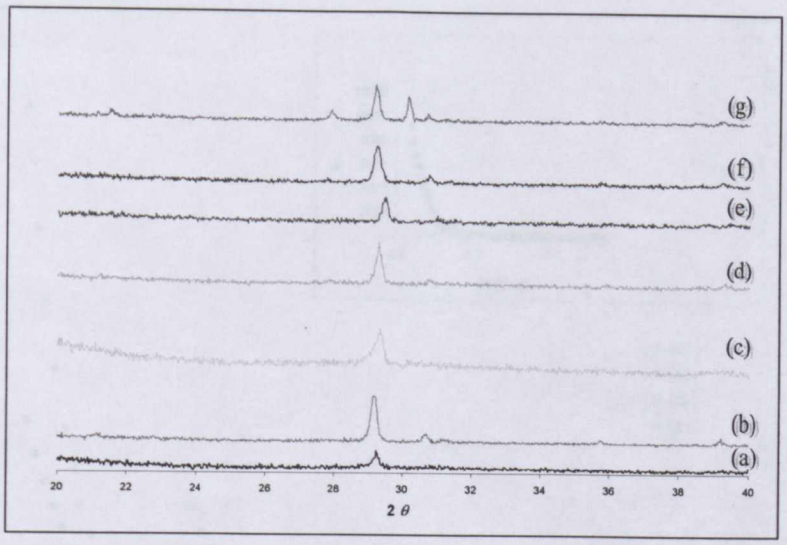

Fig. 1: X-ray diffractograms of PEMA with (a) 0, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25 and (g) 30 wt% $LiClO_4$.

The Scherrer length, L, for every sample was determined using the equation

$$L = \frac{0.9\lambda}{\Delta 2\theta_{halfpeak} \sin(\frac{2\theta_{\max}}{2})} \quad (1)$$

where $\lambda = 1.5418\,\text{Å}$ and $\Delta 2\theta$ is the width at half maximum. In this work, Scherrer length was calculated using the peak at 29.5° and it shows that the sample with 20 wt % $LiClO_4$ has the smallest value as observed in Fig. 2. According to Hashmi et.al [11], the smaller the value of L, the more amorphous the sample is. Hence the most amorphous film has ratio of 80 wt % PEMA:20 wt % $LiClO_4$.

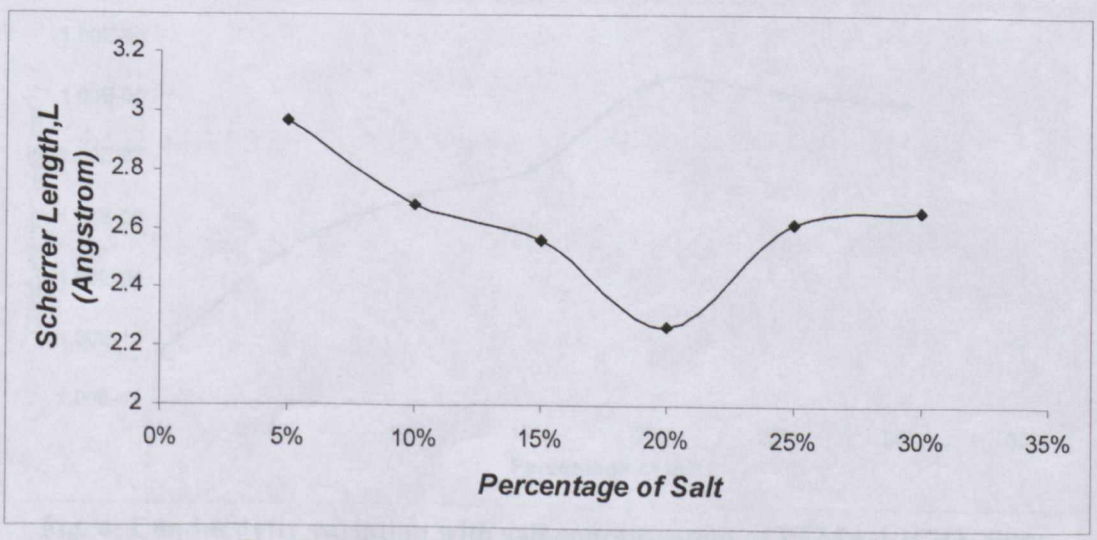

Fig. 2: Scherrer length for PEMA-$LiClO_4$ films

Graph of ε_r – log ω depicted in Fig. 3 for all films. The dielectric constant is observed to rise sharply at low frequencies. According to Mohamed and co-worker [12], this indicates that electrode polarization and space charge effects had occurred.

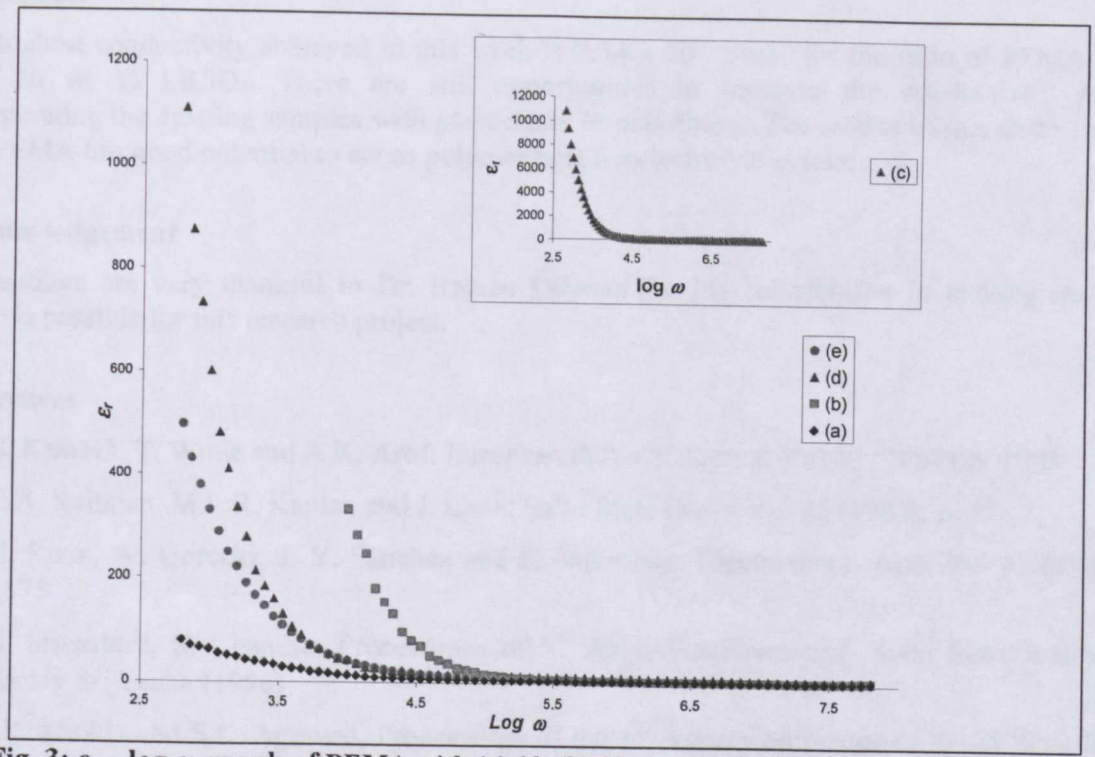

Fig. 3: ε_r – log ω graph of PEMA with (a) 10, (b) 15, (c) 20, (d) 25, (e) 30 wt% $LiClO_4$ films

Since ε_r is a reflection of the number of charge carriers present, hence it can be inferred that the sample with 20 wt % $LiClO_4$ has the highest number of charge carriers and is expected therefore to have the highest conductivity. This is supported by the graph shown in Fig. 4 which shows the variation of conductivity with salt concentration at room temperature. From Fig. 4, the highest conductivity obtained is 2.34×10^{-6} S cm^{-1} for the sample with 20 wt % $LiClO_4$. This is comparable to the value of conductivity obtained for other dry polymer electrolytes reported in the literature [13,14,15]

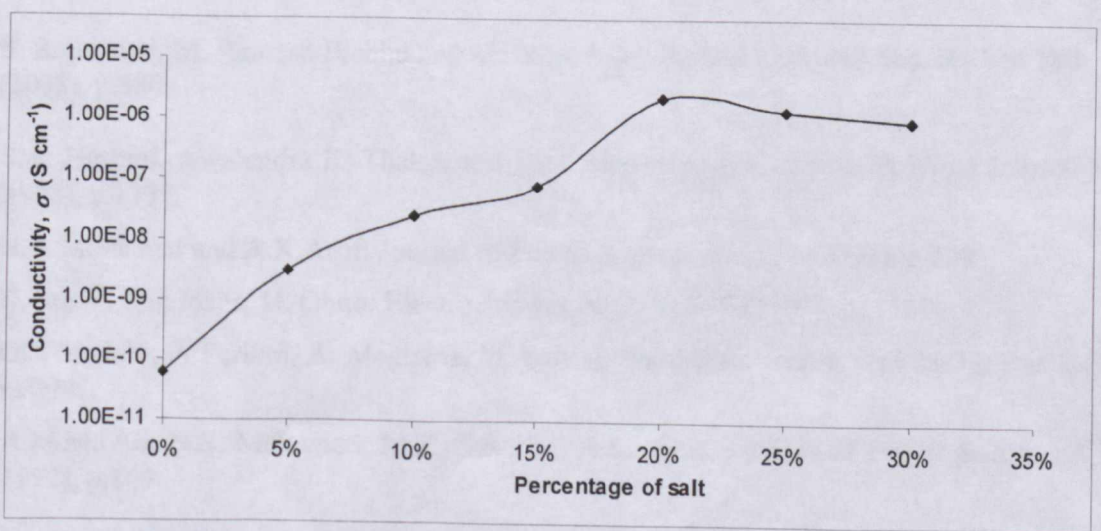

Fig. 4: Conductivity variation with salt concentration of PEMA-$LiClO_4$ films

Fig. 4 also shows that the conductivity decreases for films with more than 20 wt % $LiClO_4$. This is attributed to the decrease in the fraction of amorphous region and decrease in the number of charge carriers as indicated in Fig. 2 and Fig. 3 respectively.

Conclusion

The highest conductivity achieved in this work is 2.34 x 10^{-6} Scm^{-1} for the ratio of PEMA added with 20 wt % $LiClO_4$. There are still opportunities to increase the conductivity perhaps incorporating the existing samples with plasticizers or nanofillers. The results of this study indicate that PEMA has good potential to act as polymer host for electrolyte systems.

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